

FLUORODINITROETHANOL AND DERIVATIVES*

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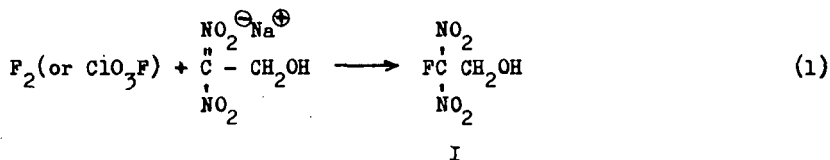
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Introduction

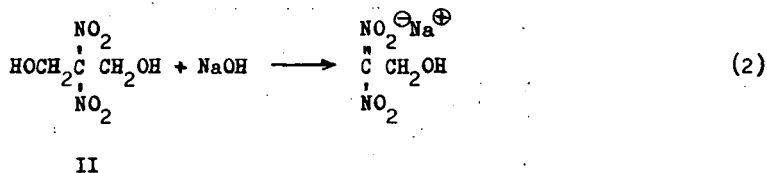
The chemistry of 2-fluoro-2,2-dinitroethanol has been investigated for the past several years, and it is a privilege to present some of this material at this time. This paper presents a summary of a process evaluation study, and much of the chemistry involved will be reported in greater detail by the original authors in the coming months. It may be stated at the outset that the chemistry of fluorodinitromethyl compounds shows marked similarity to trinitromethyl or *gem*-dinitromethyl compounds, which are well-known in the literature.

Synthesis of 2-Fluoro-2,2-dinitroethanol

One preparative method for 2-fluoro-2,2-dinitroethanol (FDNE) is based on the fluorination of the aci-sodium salt of dinitroethanol



The starting material for Reaction (1) is prepared *in situ* by the deformation of 2,2-dinitro-1,3-propanediol with one mole of base



Compound II is preferably prepared by the oxidative nitration of 2-nitro-1,3-propanediol (Reference 1). II is not isolated, but is partially purified by extraction from the aqueous reaction mixture with ethyl or isopropyl ether, followed by an extraction of the ether solution with aqueous base, which converts II to the aci-sodium salt of dinitroethanol. Although other methods of preparation of II are known, the route shown was the one of choice.

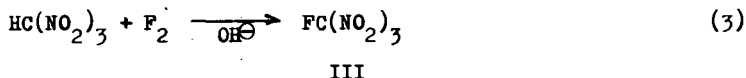
Conversion of II to FDNE was carried out by introducing fluorine gas, diluted 1:1 with nitrogen, into the aqueous solution of the aci-sodium salt at 15 to 25° (Reference 2). It was found that efficient dispersion of the fluorine is essential, and that stainless steel gas-inlet tubes with open ends of 1/4 or 3/8 in., or with various hole sizes of 0.016 to 0.040, are satisfactory in a 50-liter vessel. The smaller the diameter of the holes, however, the more frequently were they occluded by sodium fluoride. A rapid injection of water served to remove the obstruction.

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Yields of 60 to 70% of FDNE were generally obtained, although about 100% of the theoretical quantity of fluorine was consumed. The pH of the solution was not a critical factor, so long as it was maintained at or above the 7.5 to 8.0 level. The same results were obtained whether the pH was maintained at 8.0 or whether fluorination was begun at a pH of about 11, and the solution allowed to go acid; in the latter case, however, it was sometimes necessary to add alkali and to continue the fluorination.

Ethyl ether was found to be very efficient in extracting FDNE from the aqueous fluorination mixture. However, it tends to extract some impurities along with the FDNE. For example, one of the contaminants found in the fluorination of II was identified as 2,2,4,4-tetranitro-1,5-pentanediol (Reference 3). It was obtained in rather significant quantity (3 to 5 percent) from an ether extract of FDNE, from a batch in which most of the FDNE had previously been extracted with methylene chloride. In actual practice, sodium chloride is added to decrease the solubility of FDNE in the aqueous medium, and methylene chloride, with a far less favorable distribution coefficient than ether, is used as the extractant. The crude product obtained by removing the solvent is generally 80 to 90 mole-percent pure, as analyzed by gas chromatography.

An alternate method for preparing FDNE consists of the fluorination of nitroform, followed by reduction with alkaline peroxide and the Henry reaction with formaldehyde (References 2 and 4).



The fluorination of nitroform is carried out under conditions similar to those described for the aci-sodium salt of dinitroethanol, but the yields are superior (80 to 90% of theory), and the isolation of the product presents little difficulty; III is essentially insoluble in water, and, following mild washing, is obtained in 98 mole-percent purity (gas chromatography). A slight source of difficulty is presented by the emulsified interface, but this problem can be overcome by vacuum filtration and water-washing. Nitroform starting material may, if necessary, be prepared by the alkaline-peroxide reduction of tetranitromethane, and fluorinated in situ; in this case, yields of III from 65 to 70% (based on tetranitromethane) are obtained.

The route shown in (4) was discovered by workers at the U.S. Naval Ordnance Laboratory and substantial improvements since then, primarily by NOL, have made the process a very attractive one. The reduction of III, when carried out at -5 to -10°C in alkaline medium with a 20% excess of hydrogen peroxide and formaldehyde, gives yields of 90% FDNE in 95 mole-percent purity. The reaction can be effected in aqueous methanol in order to enhance the solubility of FTM in the reaction mixture, or, alternatively, a surface-active agent such as sodium p-toluenesulfonate or Triton X-100*, may be added to achieve the same result. The latter method is particularly advantageous when it is desired to use the solution of FDNE in the methylene

* An alkyl phenoxy polyethoxyethanol (Rohm & Haas Co.)

chloride extractant without other hydroxyl-containing impurities; water alone is readily removed from the solution, but a significant quantity of methanol, together with the attendant water, presents a more tedious problem.

Physical Characteristics of FDNE

Fluorodinitroethanol is a mobile, colorless liquid, b.p. 53° at 1 mm Hg, m.p. 9 to $10\text{--}1/2^{\circ}\text{C}$. Its density is 1.54 g/cc at 25°C . It can be vacuum-distilled with very minor decomposition (much less than 1%), but that slight decomposition does occur is indicated by small deposits of paraformaldehyde. Its refractive index is 1.4330 (n_D^{25}). It is a very strong vesicant, and skin contact is to be avoided. Values of its sensitivity to impact or shock are not very consistent, but certain evidence suggests that caution is in order. For example, a 70 weight-percent solution in methylene chloride had an impact sensitivity of less than 10 cm compared to 50 cm for neat FDNE (Olin Mathieson Tester, 2 Kg weight, 50% point; n-propyl nitrate = 8 cm).

Analysis of FDNE

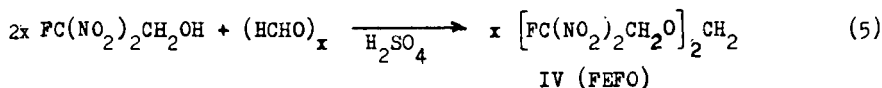
Analysis of FDNE may be based on several criteria, of which purity by gas-chromatography is perhaps the most useful. Consistent results have been obtained with a 6-ring polyphenyl ether column in an Aerograph A90 gas chromatograph. An Aerograph Model 325 temperature programmer was attached to the oven heater, and by programming from 90 to 140°C at $6^{\circ}\text{C}/\text{min}$, very satisfactory separation of components was achieved.

FDNE may also be analyzed by measuring its absorbancy in dilute aqueous base at 382 m μ . For pure FDNE, $\log \epsilon = 4.27$. This determination must be made on fresh solutions, as the anion of fluorodinitromethane reacts with hydroxide ion.

A third method of analysis was developed by titration of FDNE in acetonitrile with 0.1N tetrabutylammonium hydroxide. Under these conditions, FDNE titrated as a dibasic acid, giving a single, sharp inflection.

Synthesis of bis(2-Fluoro-2,2-dinitroethoxy)methane

One of the more interesting derivatives of FDNE is its formal, bis(2-fluoro-2,2-dinitroethoxy)methane (FEFO) (Reference 5). Since conventional methods of acetal formation fail with electronegatively substituted alcohols such as trinitromethyl, gem-dinitro, and fluorodinitromethyl compounds, recourse was had to a method first developed at NOL (Reference 6), involving the use of concentrated sulfuric acid as the reaction medium



Under these conditions, FEFO is produced in 70 to 90% yields. The reaction may conveniently be carried out by adding concentrated sulfuric acid slowly to a solution of FDNE and g-trioxane in methylene chloride, but many variations yield equally satisfactory results. In place of trioxane, paraformaldehyde may be used, and the methylene chloride may be replaced by a similar solvent, or the reaction may be effected without the use of organic solvent by adding FDNE to a solution of formaldehyde (from either trioxane or paraformaldehyde) in sulfuric acid. A solvent may then be employed to assist in the isolation and purification of the product.

The effects of an excess of formaldehyde or an excess of FDNE on the yield and purity of FEFO were assessed in a series of runs in which the molar ratios of FDNE to formaldehyde were 2.5:1.0, 2.0:1.0, and 1.5:1.0, respectively. An additional run was made at the 2.0:1.0 ratio, in which the condensation medium was 100% sulfuric acid in place of the usual 95 to 98% acid. The results are summarized in Table 1.

TABLE 1

VARIATION OF REACTANT RATIO IN FEFO SYNTHESIS

Case No.	Molar Ratio, FDNE:HCHO	% FEFO*	% Impurity of Higher GC Retention Time	% Yield
1	2.5:1.0	99.2	0.8	88.0
2	2.0:1.0, conc H ₂ SO ₄	98.2	1.8	82.9
3	2.0:1.0, 100% H ₂ SO ₄	98.9	1.1	79.0
4	1.5:1.0	93.6	6.4	83.5

* GC assay

It is apparent that the reagents in stoichiometric ratio will yield good FEFO very effectively; that the higher purity FEFO obtainable with 100% sulfuric acid may compensate for the use of slightly less pure FDNE; and that even a 25% excess of formaldehyde can be tolerated, provided purification with sulfuric acid is added to the process (see below).

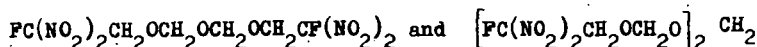
A series of runs (all with molar ratio 2.0:1.0) in which the reaction temperature was maintained for two hours at 0 to 10°C, 20 to 25°C, and 35 to 40°C, gave yields of 87.3, 87.8, and 84.0% FEFO, respectively, all of identical quality. The run at the highest temperature was carried out primarily to determine what, if anything, might occur if the reaction went out of control. Since methylene chloride served as the organic solvent in these runs, it apparently served to control the exotherm. This series further showed that product yield and purity are unaffected by reaction temperatures from 0° to at least 25°C.

In practice, the preparation of FEFO can be carried out conveniently by using the solution of FDNE in methylene chloride directly, without isolating the FDNE, although the solution is generally dried by passing through a silica gel-Drierite column, and a portion of the solvent is removed by distillation to avoid handling excessive volumes. The requisite amount of *g*-trioxane is then added to the solution, and concentrated sulfuric acid (approximately 1 ml acid per gram of FDNE) is then added dropwise with good agitation at 20 ± 5°C. The reaction mixture is stirred an additional 1 to 2 hours, and the methylene chloride (upper) layer is separated. The FEFO solution is then washed countercurrently or batchwise with 5% aqueous sodium hydroxide, and dried by percolation through a column of silica gel. Removal of the solvent under vacuum leaves the product as a clear, colorless liquid, generally 90 to 98 mole-percent pure, as analyzed by gas chromatography.

The contaminants in FEFO generally consist of several products of lower GC retention-times, and one or two of higher retention times.* The latter have been

* Referred to, for convenience, as "high-boilers"

identified (Reference 7) as the FEFO analogs with two and three methyleneoxy chains in the molecule, respectively.



V

VI

Compounds V and VI seem to arise whenever the condensation medium is contaminated with water. If one is aware of this beforehand, the problem can be overcome by the use of fuming sulfuric acid, as shown in Table 2.

TABLE 2
EFFECT OF DILUTION WITH WATER ON FEFO SYNTHESIS

Case No.	Conditions	Mole-% Components with lower GC retention time	% FEFO	% High-boilers	% Yield
5	Standard*	3.6	93.4	3.0	92.5
6	10% H ₂ O added to FDNE	4.3	44.7	51.0	83.6
7	As in 93, with 20-23% fuming H ₂ SO ₄ in place of conc. H ₂ SO ₄	2.9	93.4	3.7	77.7

* 2.0 moles of FDNE (distilled) per mole of formaldehyde

Results similar to those of Case No. 6 are obtained whenever the FDNE-methylene chloride solutions are inadequately dried.

If the FEFO product is still too highly contaminated with V and/or VI, purification may be effected by low-temperature crystallization from methylene chloride-hexane in a tedious, somewhat wasteful procedure, or by agitation with concentrated sulfuric acid. Results from the latter treatment are presented in Table 3.

TABLE 3
PURIFICATION OF FEFO WITH SULFURIC ACID

Case No.	Mole-% Components with lower GC retention time	% FEFO	% High-Boilers		% Recovery
			V	VI	
8, crude	1.2	87.3	5.6	5.9	-
8, purified	1.7	96.6	0.1	1.6	82
9, crude	0.7	95.6	3.7	-	-
9, purified	1.4	98.6	-	-	89

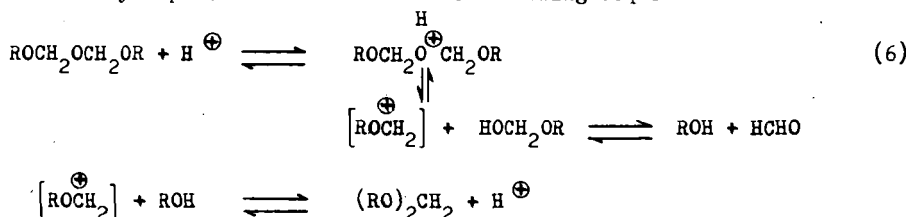
Extremely interesting results were obtained in the course of preparing FEFO from an FDNE-methylene chloride solution after attempted purification. This FDNE was prepared from fluorotrinitromethane in methanolic solution, and the FDNE-methylene chloride solution was later found to be highly contaminated with methanol and water. The crude FEFO-methylene chloride solution, following separation from the sulfuric acid layer, was divided into two equal portions. One portion was worked up in the usual manner, and the other was treated with two portions of concentrated sulfuric

acid before being worked up. The first portion gave a yield of 48 percent (calculated as FEFO), the second 42 percent. GC analysis showed the following results:

TABLE 4

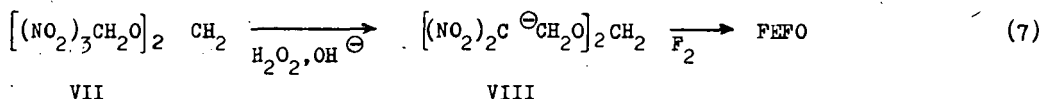
Case No.	IN-PROCESS PURIFICATION OF FEFO WITH SULFURIC ACID		% High-Boilers	
	Mole-% Components with lower GC retention time	% FEFO	V	VI
10, treated as usual	17.1	37.6	43.8	1.5
10, purified in process	1.0	93.7	5.3	-

In spite of the fact that the conventionally-treated FEFO was apparently not completely freed of solvents, and the results are thus not strictly comparable, it is evident that a very high degree of purification was achieved. Since the yield of FEFO was nearly the same in both cases, it must be concluded that purification took place primarily other than through extraction of V and VI, and that the latter may have been converted into FEFO by a process indicated in the following sequence:



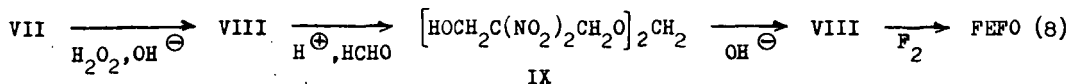
The purification of FEFO with concentrated sulfuric acid immediately following separation of the FEFO-methylene chloride solution from the sulfuric acid reaction medium has consistently removed nearly all of the high-boiling contaminants, and has been made a standard procedure in FEFO preparation.

Several routes are known which yield FEFO from intermediates other than FDNE. One of these methods utilizes bis(2,2,2-trinitroethoxy) methane (VII) as the starting material (Reference 4)



VII is reduced to the disodium salt (VIII) in the presence of alkaline peroxide in aqueous methanol. The organic solvent, added initially to ensure solubility and facilitate reaction of the starting material, must then be removed by vacuum distillation prior to fluorination. The product has been obtained in yields of up to 60% by this route. The sensitivity of VII, and the fact that large volumes and much time are required to effect the removal of the methanol, are severe disadvantages in this process.

Moderate yields of pure FEFO are obtained via another route which utilizes VII as the starting material:



The conversion of VIII, by means of the Henry reaction, to bis(3-hydroxy-2,2-dinitropropoxy)methane serves as a means of purification, and as a result the yields from IX

to FEFO are quite high (80 to 85%). The overall yield starting from VII, however, is 45 to 55%, and the large volumes and lengthy procedures decrease the utility of this method even further.

Physical Characteristics of FEFO

FEFO is a colorless liquid, b.p. 120 to 124°C at 0.3 mm Hg, m.p. 14°C. Its density is 1.595 g/cc at 25°C, and its index of refraction $n_D^{25} = 1.4398$. It is soluble in the lower aliphatic alcohols and esters, and in most chlorinated solvents. It is stable to strong acids, and relatively stable to dilute aqueous alkali. Its sensitivity to impact has given values ranging from 11 cm (50% point, 2 Kg weight, RDX = 28 cm) to 40 to 50 cm (50% point, 2.5 Kg weight). Toxicity data are scanty but tend to indicate relatively low toxicity, at least by external exposure to skin or eye.

Analysis of FEFO

Gas chromatography has been employed as the most suitable analytical method for FEFO assay. GC FEFO analyses are conducted with a six ring polyphenyl ether column and a sensitive flame ionization detector. A 2-minute isothermal run at 100°C is followed by a programmed increase of 6°C/minute to 200°C, and an additional 8 minutes at 200°C. All components are eluted within a 20-minute period. These operating conditions give well-resolved peaks with minimal tailing. Although sample sizes have been varied between 0.2 and 0.8 μ l, 0.2 to 0.3 μ l is preferred.

Preliminary studies suggested that chromatograph oven temperatures between 180 and 200°C would not cause measurable decomposition of FEFO. Therefore, to enhance volatilization and peak shape, a pre-heater temperature of 185°C was selected. However, at this temperature the area percents of the more volatile components did not reproduce well, although consistent data were obtained for the other impurities. A later series of tests of vaporizer temperatures from 150 to 200°C demonstrated the necessity of operating at 150°C because of an apparent degradation of FEFO at the higher temperatures. The data suggest that the apparent increase in impurities of low retention time at temperatures above 150°C is actually due to degradation of FEFO. Its assay decreases with the increase of these impurities attendant with the increased temperatures. By operating the vaporizer at 150°C, reproducible chromatograms are obtained without noticeably altering the elution times.

The anhydrous potentiometric titration applicable to FDNE may be used for FEFO also. FEFO can be titrated in acetonitrile with tetrabutylammonium hydroxide to give a single well-defined break corresponding to the removal of four protons per mole. A single sample assayed 88.8% FEFO, compared with 86.7% obtained by gas chromatography. Since the impurities in FEFO are also apt to have acidic properties, this method was not developed further.

Acknowledgment

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